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BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mm/min	millimeter per minute
g/cm^3	gram per cubic centimeter	mol/L	mole per liter
kg	kilogram	mPa	megapascal
kW	kilowatt	mV	millivolt
L	liter	pct	percent
μm	micrometer	ppm	part per million
min	minute	rpm	revolution per minute
mL/min	milliliter per minute	yr	year
mm	millimeter		

ZERO-SURFACE-CHARGE-CONTROLLED DRILLING FOR ENHANCED PENETRATION AND EXTENDED BIT LIFE

By John E. Pahlman,[1] William H. Engelmann,[2]
Patrick A. Tuzinski,[3] and Pamela J. Watson,[4]

ABSTRACT

The U.S. Bureau of Mines has continued its investigation of chemical additive drilling fluids that produce a zero surface charge (ZSC) on a rock to better define the boundary conditions of the phenomenon. Laboratory drilling tests were performed on Minnesota taconite, Tennessee marble, and Sioux Quartzite using diamond-impregnated coring bits or tungsten carbide spade bits. Drilling fluids were made from chemical additives such as inorganic salts, cationic surfactants, cationic polymers, acids, or nonionic polymers in either distilled, deionized water (DDIW), mine pond water, mine well water, or tap water. These additives were tested below, at, and above their respective ZSC concentrations. Penetration and bit life improvements obtained with ZSC concentration solutions ranged from 88 and 56 pct, respectively, to over 650 pct and over 400 pct, respectively, for the additives tested. Polyethylene oxide (PEO) was found to be the best additive for ZSC-controlled drilling because a continuous range of PEO solution concentrations produced the enhanced ZSC-controlled drilling performance.

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INTRODUCTION

Watson (*1*)[5] surveyed and summarized 60 yr of literature-reported results of using chemical additives in rock fragmentation processes. In that 60-yr period, several researchers reported significant increases in the drilling performance with the addition of additives to the drilling fluid, while others reported no beneficial effect. Some noteworthy successes include Rehbinder's work (*2*), in which drilling efficiency increases of up to 60 pct were obtained; Shepherd's work (*3*), in which slightly less increase in drilling efficiencies was obtained; and Westwood's work (*4*), which indicated that drilling efficiency could be improved well over 100 pct. The survey showed that, while the use of chemical additives in the drilling fluid was sometimes beneficial, little scientific reasoning was provided in the literature to explain either the presence or absence of beneficial effects when using these chemical additives. Usually, only very general ideas were reported. In many cases, the experimentation was terminated before a conclusive proof-of-effect could be confirmed.

The Bureau has designed and conducted laboratory drilling studies to establish and understand the necessary boundary conditions for chemical control of drilling performance. Two recent reports (*5-6*) have identified establishment of a zero zeta potential or ZSC condition for the rock as the fundamental condition necessary for successful drilling performance improvement. Using the chloride salts of aluminum ($AlCl_3$), calcium ($CaCl_2$), sodium (NaCl), and zirconium ($ZrCl_4$), as well as aluminum nitrate ($Al(NO_3)_3$), at their respective ZSC concentrations, drilling performance in Sioux Quartzite, Westerly Granite, and Minnesota taconite was greatly improved. Not only was penetration enhanced (sometimes by as much as 150 pct), the bit life was also simultaneously extended (again, sometimes by as much as 150 pct).

This paper describes research conducted subsequently to further determine the boundary conditions under which drilling performance can be improved by maintaining the ZSC condition. The objects of this research were to determine the universality of the phenomenon with respect to (1) rock type, (2) bit type, (3) surface charge (zeta potential) modifier, and (4) drilling fluid water.

ROCK MATERIALS USED IN TESTS

All rock samples were wire sawed into 15-cm cubes for the drilling tests. Rock fragments were reduced to minus 149 μm for the zeta potential measurements and chemical analyses. The physical properties of these rocks are given in table 1.

TENNESSEE MARBLE

Tennessee marble (quarry trade name) used in this investigation came from the Holston Limestone formation in the Great Valley of east Tennessee (*7*). The formation is an essentially unmetamorphosed, coarsely crystalline limestone of Middle Ordovician Age. The formation shows a range of colors from light gray to pinks and red to dark brown. Dark gray stylolitic seams are characteristic features, and often separate one color from another.

The Holston Limestone was deposited as a fossil hash of shells and shell fragments. After deposition, the beds were buried, compacted, and lithified. Later tectonic activity resulted in folding, faulting, regional uplifts, and partial recrystallization to a fabric of twinned calcite grains that enclose and replace fossil fragments (*7*). A bulk rock sample was obtained from one of the active quarries in the Knoxville area. Chemical analyses for this sample are given in table 2.

[5]Italic numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1.—Physical properties of test rocks (*7*)

Property	Tennessee marble	Minnesota taconite	Sioux Quartzite	
			Reference	This report
Porosity . . . . . pct . .	0.17	ND	0.14	ND
Density . . . . . g/cm^3 . .	2.70	3.23	2.64	ND
Strength, MPa:				
Compressive	118.0	443.0	505.0	499±47.9
Tensile	10.1	26.3	10.8	21.6±3.8

ND Not determined.

TABLE 2.—Chemical analyses for Tennessee marble

Compound	pct
SiO_2	<0.21
Al_2O_3	.23
FeO	ND
Fe_2O_3	.21
$MgCO_3$	.76
$CaCO_3$	97.39
Na_2CO_3	<.67
K_2CO_3	<.06
TiO_2	<.33
P_2O_5	.30
$MnCO_3$	.03
$BaCO_3$	<.11
Li_2O	<.22
H_2O^- LOI at 105° C	<.10
H_2O^+ LOI at 1,000° C	ND

LOI Loss on ignition. ND Not determined.

MINNESOTA TACONITE

The taconite used in this investigation was a dark green to gray, fine-grained, metasedimentary rock from Minnesota's Mesabi Iron Range. It consisted of chert, magnetite, hematite, siderite, and the following silicates: minnesotaite, greenalite, stilpnomelane, and amphibole. The taconite has mildly undulating black bands of magnetite that occur in irregular layers, which accounts for the overall 27 to 30 pct iron content. The taconite was provided by Erie Mining Co., located near Hoyt Lakes, MN. Chemical analyses are given in table 3.

TABLE 3.—Chemical analyses of Minnesota taconite, from blasthole drill cuttings, area 9, Erie Mining Co. (LTV Steel) open pit, Hoyt Lakes, MN, percent

Compound	Sample A, Nov. 1985	Sample B, Nov. 1985	Sample C, Nov. 1986
SiO_2	35.30	34.23	40.65
Al_2O_3	.30	.34	.87
FeO	22.26	24.31	14.28
Fe_2O_3	28.73	27.16	35.74
MgO	2.32	1.82	2.49
CaO	3.50	4.06	2.24
Na_2O	<.067	<.067	<.067
K_2O	<.06	<.06	<.06
TiO_2	<.33	<.33	<.33
P_2O_5	<.046	<.046	<.046
MnO	.72	.80	.90
BaO	<.11	<.11	<.11
H_2O^- LOI at 105° C	<.1	<.1	<.1
H_2O^+ LOI at 1,000° C	1.00	.60	3.40

LOI Loss on ignition.

SIOUX QUARTZITE

Sioux Quartzite used in the present study has been described in more detail in a previous report (*5*). Briefly, it is a homogeneous, fine-grained metamorphosed sandstone that has a relatively fracture-free structure. It is composed mainly of quartz grains and averages 98.5 pct silica. It was obtained from a quarry in southwestern Minnesota.

WATERS USED IN TESTS

Four waters were employed in the drilling tests: DDIW, tap water, mine pond water, and mine well water. Chemical analyses of these waters are given in table 4.

TABLE 4.—Chemical analyses of waters used in testing, parts per million

Element or compound	DDIW	Tap	Mine	
			Pond	Well
Al^{3+}	<0.02	0.06	ND	<0.01
Ca^{2+}	<.02	20.8	76.5	62.9
Mg^{2+}	<.01	6.6	45.2	34.8
Mn^{2+}	<.02	<.10	1.8	1.1
Na^+	<.5	10.8	40.0	41.7
K^+	<.5	2.2	7.4	6.5
SO_4^{-2}	<2.0	<.5	121.0	84.4
Si	.54	3.3	10.6	9.3
Cl^-	1.40	<5.0	54.5	49.3

ND Not determined.

DDIW was prepared by distilling Minneapolis tap water in a high-capacity, 200-L still and then passing it through Barnsted[6] standard and ultrapure ion exchange cartridges. The pH range of the DDIW was 5.3 to 6.0. Minneapolis tap water used in these tests had an average pH value of 7.3 to 7.7.

Both the mine pond water and mine well water were obtained from Erie Mining Co. A mine pond at the bottom of an open pit is used as a source of water during the spring, summer, and fall. A well on the property is used as a source of water in the winter. The pH of the pond water ranged from 7.0 to 7.5 and the well water pH was 7.9 to 8.0.

[6]Reference to specific products does not imply endorsement by the Bureau of Mines.

ZETA POTENTIAL MEASUREMENTS AND ZSC CONCENTRATIONS

The procedure used for measuring zeta potentials and determining the ZSC concentration is quite extensively described elsewhere (*5, 8*). Briefly, zeta potentials are determined for the rock particles in water (i.e., DDIW, tap, or mine water) and increasing concentrations of additive solutions using a zeta reader.

The zeta reader operates on the principle of electrophoretic mobility, whereby the speed of a particle in an electric field is proportional to its surface charge. The apparatus employs a video display to monitor particle movement in the electric field. When the speed of a moving grid line on the video display is matched to that of the particle, the zeta potential of that particle is shown on a digital readout.

A series of additive concentrations were tested to generate both negative and positive zeta potential values needed to graphically determine the ZSC concentration (the concentration where the zeta potential or surface charge of the rock particles is zero). ZSC concentrations were substantially different for each rock tested depending both on the additive and type of water used. Table 5 lists the ZSC concentration, as well as the zeta potentials in water alone, for all the rock-cationic additive sets tested in the drilling experiments. Table 6 lists the ZSC results for Sioux Quartzite and Minnesota taconite with PEO.

DRILLING SYSTEM

The drilling apparatus employed in this investigation is shown in figure 1. A detailed description of the mechanical and electronic components of the drilling apparatus and the drilling procedure are given in a previous report (*5*). Briefly, drilling tests were performed on 15-cm rock cubes using a 1.12-kW drill press, fitted with a water swivel and either a 16-mm-OD (10-mm-ID) diamond-impregnated coring bit or a tungsten carbide water-cooled spade bit (same diameter).

The coring bit matrix is 100 pct cobalt (powder) sintered to a Rockwell C hardness of 18 to 21. The diamonds in the matrix are quoted by the manufacturer to be minus 425 plus 300 μm. Some variation from that was found: some diamond pieces ranged from minus 1,000 plus 250 μm.

The diamond-impregnated coring bits were rotated at 100 rpm under a thrust of 150 kg; the spade bits were also rotated at 100 rpm but under a lower thrust of 60 kg. Drilling fluid was flushed through either drill at a rate of 150 mL/min. Drilling was done perpendicular to the bedding plane where applicable. The tungsten carbide spade bits were only used to drill the Tennessee marble. The bits featured replaceable, resharpenable blades with two waterways. Assembled, they resembled a machinist straight-fluted type bit. The tip had a 125° included angle, a 125° chisel angle, and a 5° to 8° negative axial rake angle.

TABLE 5.—Zeta potential results using cationic additives

Additive tested	Zeta potential of rock in water, mV	ZSC concentration, mol/L
MINNESOTA TACONITE IN DDIW		
$AlCl_3$	-17.29	1.20×10^{-6}
TENNESSEE MARBLE IN DDIW		
$AlCl_3$	-7.94	1.93×10^{-6}
SIOUX QUARTZITE IN DDIW		
DTAB	-22.40	9.35×10^{-4}
TTAB	-20.72	7.23×10^{-5}
HTAB	-22.83	1.56×10^{-6}
MINNESOTA TACONITE IN MINE WELL WATER		
Percol 402	-35.20	[1]0.64
SIOUX QUARTZITE IN TAP WATER		
PAA	-43.56	[1]0.25
$AlCl_3$	-33.00	4.50×10^{-5}
SIOUX QUARTZITE IN pH-ADJUSTED TAP WATER		
$AlCl_3$	-26.53	1.80×10^{-4}

$AlCl_3$ Aluminum chloride.
DTAB Dodecyltrimethyl ammonium bromide.
HTAB Hexadecyltrimethyl ammonium bromide.
PAA Polyacrylamide.
TTAB Tetradecyltrimethyl ammonium bromide.
[1]Part per million.

TABLE 6.—Zeta potential test results using PEO

Additive conc, ppm	Zeta potential, mV
Sioux Quartzite in tap water:	
Tap water	-33.01
1.0	-11.25
3.0	-1.18
7.48[1]	.00
12.4	.00
122.0	.00
Minnesota taconite in mine pond water:	-40.68
1.0	-10.29
3.0	-2.37
7.48	-2.29
12.4[2]	.00
122.0	.00

[1]Onset of ZSC condition between 3.0 and 7.48 ppm.
[2]Onset of ZSC condition between 7.48 and 12.4 ppm.

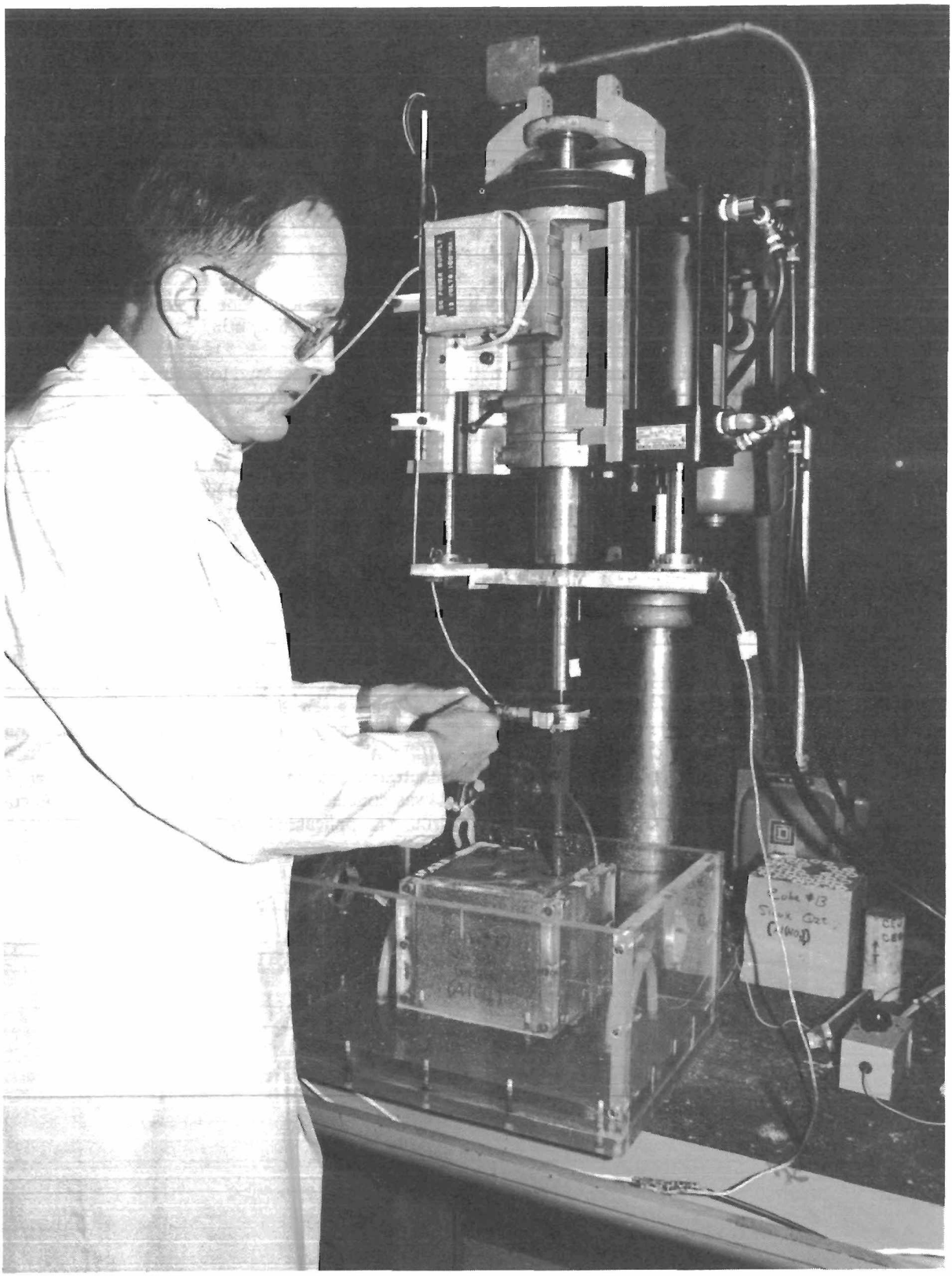

Figure 1.—Drilling apparatus.

The diamond-coring drill bits were sharpened by briefly drilling into a superduty fireclay brick (53 pct SiO_2, 42 pct Al_2O_3) to produce a sharpness level corresponding to an initial penetration rate of 4.5 mm/min in the test rock sample. The tungsten carbide blades were factory sharpened to a uniform degree; therefore, they were not resharpened in the laboratory. Drilling continued for a sequence of several holes until the average penetration rate had dropped to 2.0 mm/min in the test rock sample. The diamond-coring drill bits were resharpened before another test began; the tungsten carbide blades were simply changed for the next test.

Data on total penetration and elapsed time of drilling in progressing from the sharp bit state of 4.5 mm/min to the dull bit state of 2.0 mm/min were recorded, summed, and then used for test comparisons. The enhanced penetration performance of the additive, as compared to the appropriate baseline water was calculated by

$$E_p = [(C_p - W_p)/W_p] * 100, \quad (1)$$

where E_p = penetration effect for a test, pct,

C_p = total penetration for drilling with a given additive, mm,

and W_p = average total penetration for drilling with the baseline water alone, mm.

The bit life effect of the additive, as compared to the baseline water, was calculated by

$$E_t = [(C_t - W_t)/W_t] * 100, \quad (2)$$

where E_t = bit life effect for a test, pct,

C_t = total time for drilling with a given additive, min,

and W_t = average total time for drilling with baseline water, min.

The results of penetration and bit life effects for additive concentrations compared to their respective baseline water tests are described in the following section.

DRILLING TEST RESULTS AND DISCUSSION

EFFECT OF ROCK TYPE ON ZSC-CONTROLLED DRILLING

Previous drilling research successfully demonstrated ZSC-controlled drilling enhancement for the high-silicate-content rocks, Sioux Quartzite and Westerly Granite (*5*). Determination of the universality of rock response to ZSC-controlled drilling required testing of rocks with moderate and low or no silicate content. Minnesota taconite was chosen to represent the moderate-silicate-content rock type, while Tennessee marble (Holston Limestone) was chosen as the representative nonsilicate rock type.

Minnesota Taconite

Penetration and bit life effects comparing drilling with DDIW to several concentrations of aluminum chloride ($AlCl_3$) are given in table 7.

Drilling with $AlCl_3$ at the ZSC concentration of 1.2×10^{-6} mol/L produced simultaneous maximum increases in penetration and bit life of 143 and 104 pct (figs. 24-34). It was concluded from these results that ZSC-controlled drilling is applicable to rocks containing moderate amounts of silicate.

TABLE 7.—Drilling results for all additives, percent

Concentration tested, mol/L	Penetration	Bit life
MINNESOTA TACONITE IN DDIW WITH $AlCl_3$		
7.0 × 10^{-7}	56.24	42.68
9.0 × 10^{-7}	53.93	28.25
1.0 × 10^{-6}	70.20	71.15
[1]1.2 × 10^{-6}	143.45	104.46
1.4 × 10^{-6}	135.55	104.07
1.7 × 10^{-6}	22.48	6.14
2.0 × 10^{-6}	34.17	37.50
TENNESSEE MARBLE IN DDIW WITH $AlCl_3$		
4.0 × 10^{-7}	15.94	39.65
1.6 × 10^{-6}	25.07	50.18
[1]1.9 × 10^{-6}	50.09	98.18
2.3 × 10^{-6}	84.25	146.09
4.0 × 10^{-6}	22.79	41.80
SIOUX QUARTZITE IN DDIW WITH DTAB		
3.0 × 10^{-4}	-32.92	-27.39
[1]9.8 × 10^{-4}	118.18	99.56
1.5 × 10^{-3}	111.36	108.41
SIOUX QUARTZITE IN DDIW WITH TTAB		
5.0 × 10^{-6}	-34.79	-33.11
9.0 × 10^{-6}	-5.82	-7.83
1.7 × 10^{-5}	-.19	-4.75
1.85 × 10^{-5}	1.08	-4.31
2.0 × 10^{-5}	13.31	-3.14
2.2 × 10^{-5}	-17.47	-11.64
2.5 × 10^{-5}	-49.15	-43.50
2.8 × 10^{-5}	-45.20	-45.60
3.0 × 10^{-5}	16.75	19.14
5.0 × 10^{-5}	-35.11	-33.51
[1]7.23 × 10^{-5}	87.84	87.02
9.0 × 10^{-5}	-6.86	22.60
SIOUX QUARTZITE IN DDIW WITH HTAB		
5.0 × 10^{-7}	9.27	1.26
9.0 × 10^{-7}	71.67	54.57
[1]1.6 × 10^{-6}	87.70	55.94
3.0 × 10^{-6}	-10.22	-10.80
5.0 × 10^{-6}	-3.94	-3.27
MINNESOTA TACONITE IN MINE WELL WATER WITH PERCOL 402		
0.40 ppm	105.66	92.30
[1]0.64 ppm	174.98	141.40
1.0 ppm	-7.73	-3.48
6.4 ppm	9.90	22.34
MINNESOTA TACONITE WITH BUFFERED pH SOLUTIONS		
7.0 pH units	31.00	54.70
6.0 pH units	138.95	129.15
[1]5.5 pH units	278.63	218.14
3.5 pH units	19.43	49.29
SIOUX QUARTZITE IN TAP WATER WITH PAA		
0.10 ppm	-16.54	-15.52
0.15 ppm	47.99	29.18
0.20 ppm	209.17	183.14
[1]0.25 ppm	334.03	187.22
0.50 ppm	174.83	124.49
1.0 ppm	26.82	22.02
SIOUX QUARTZITE IN TAP WATER WITH PEO		
1.0 ppm	66.16	45.55
[1]3.0 ppm	429.65	270.58
7.5 ppm	348.56	235.69
12.5 ppm	363.65	235.90
125.0 ppm	387.60	330.05
MINNESOTA TACONITE IN MINE POND WATER WITH PEO		
3.0 ppm	107.80	130.66
7.5 ppm	246.76	220.14
[1]12.5 ppm	647.52	421.28
125.0 ppm	661.94	603.67
[2]SIOUX QUARTZITE IN TAP WATER (pH = 3.8) WITH $AlCl_3$		
7.0 × 10^{-7}	45.37	16.07
1.0 × 10^{-4}	46.20	49.78
1.15 × 10^{-4}	46.27	20.23
1.175 × 10^{-4}	80.51	48.97
1.6 × 10^{-4}	80.74	66.31
1.7 × 10^{-4}	95.82	34.06
[1]1.8 × 10^{-4}	113.63	59.59
1.9 × 10^{-4}	97.02	76.94
2.0 × 10^{-4}	33.06	6.47
3.0 × 10^{-4}	-26.82	-29.30

[1]Zero surface charge concentration. [2]Compared to baseline water of same pH 3.8 level.

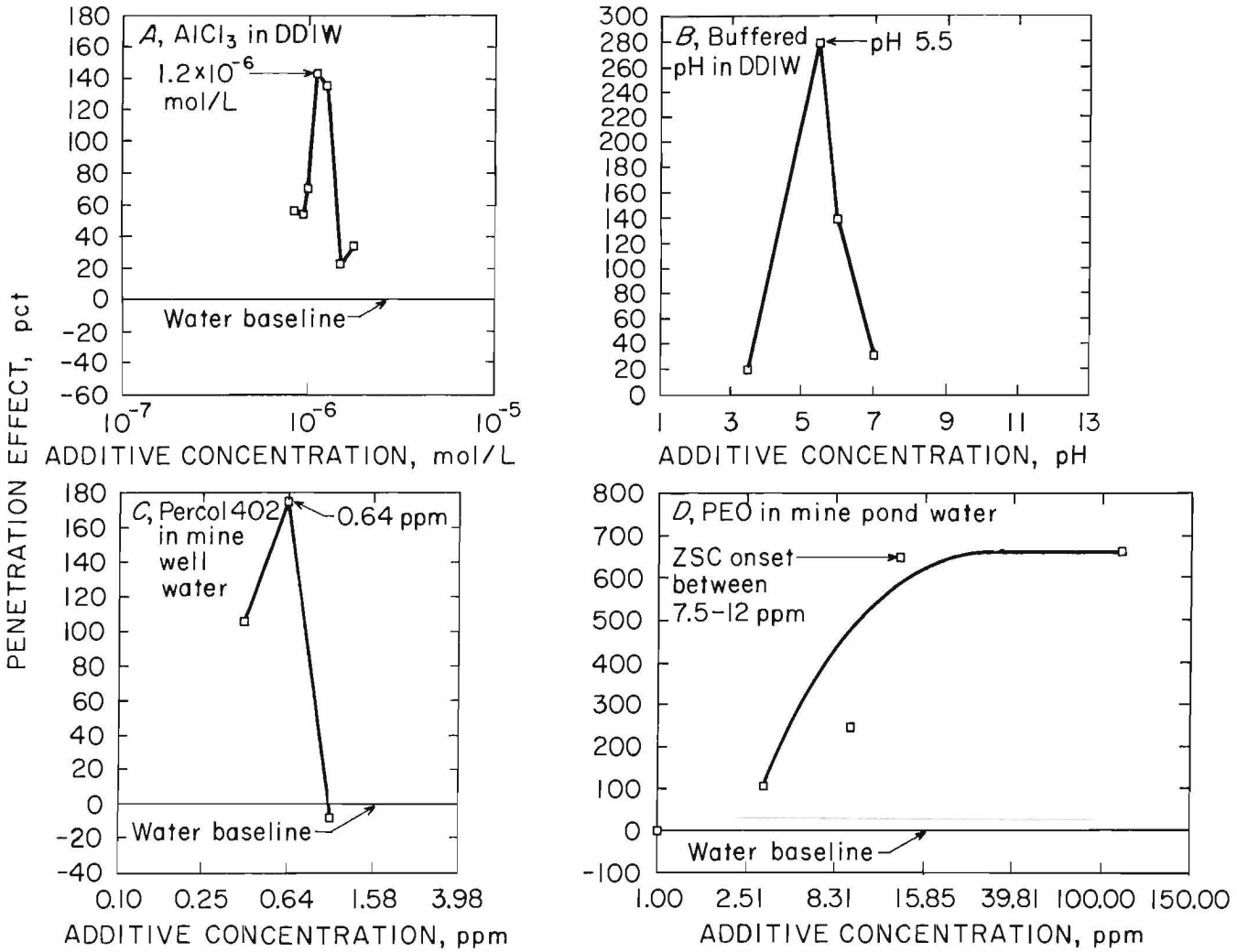

Figure 2.—ZSC control of drilling penetration in Minnesota taconite with $AlCl_3$ and acid in DDIW, Percol 402 in mine well water, and PEO in mine pond water.

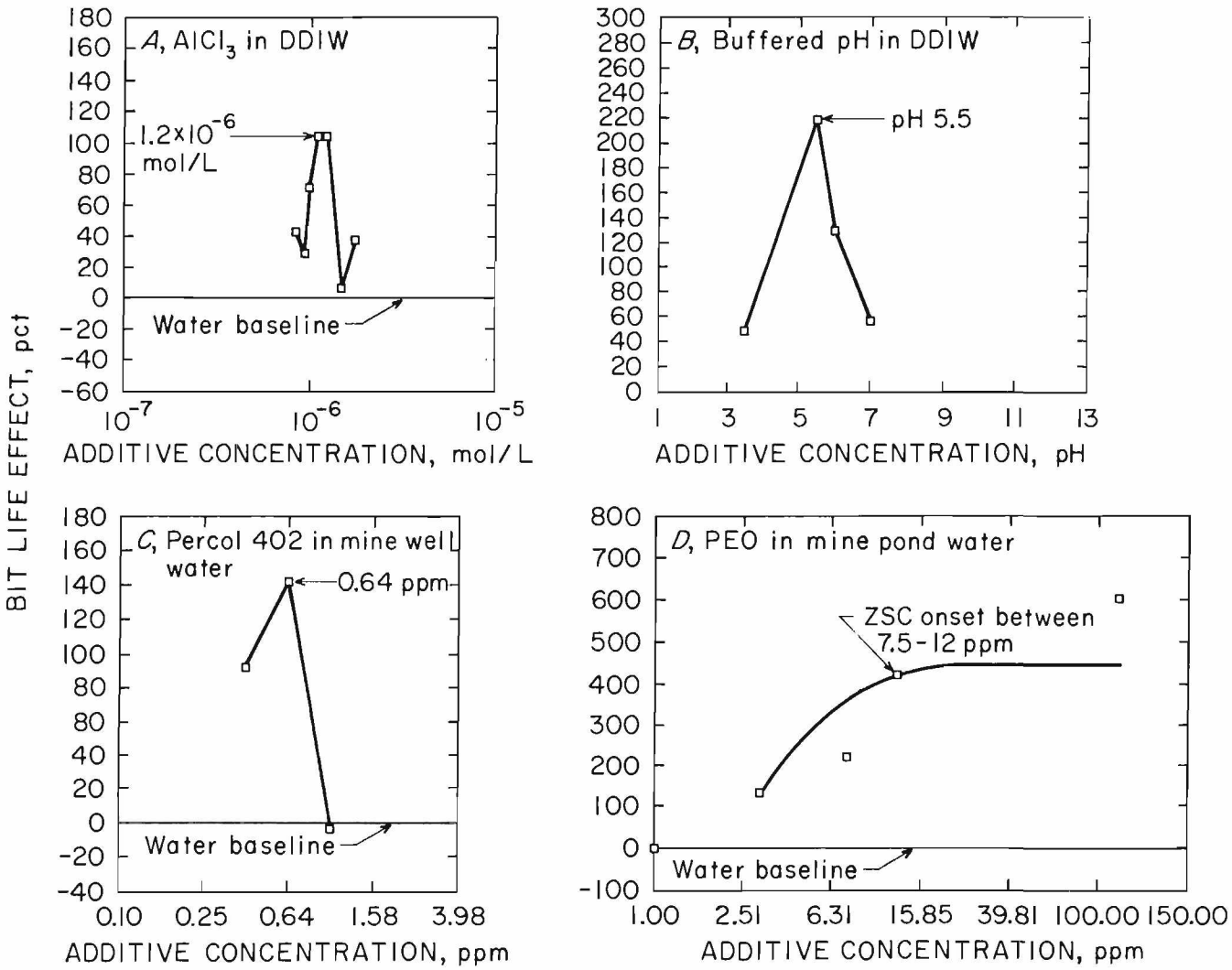

Figure 3.—ZSC control of bit life in drilling Minnesota taconite with $AlCl_3$ and acid in DDIW, Percol 402 in mine well water, and PEO in mine pond water.

Tennessee Marble

Penetration and bit life effects comparing drilling with DDIW to several concentrations of $AlCl_3$ are given in table 7. The drag, or spade-type, bit was used only for drilling into this rock type. Drilling with $AlCl_3$ at 2.3 $\times 10^{-6}$ mol/L, very near the ZSC concentration of 1.93 $\times 10^{-6}$ mol/L, resulted in a peak increase in penetration improvement of 84 pct and a bit life extension of 146 pct (fig. 4).

It is concluded from the results for Minnesota taconite and Tennessee marble, and from previous drilling test results for Sioux Quartzite and Westerly Granite, that ZSC-controlled drilling should be universally applicable to all rock types whether they have high, moderate, low, or zero silicate content.

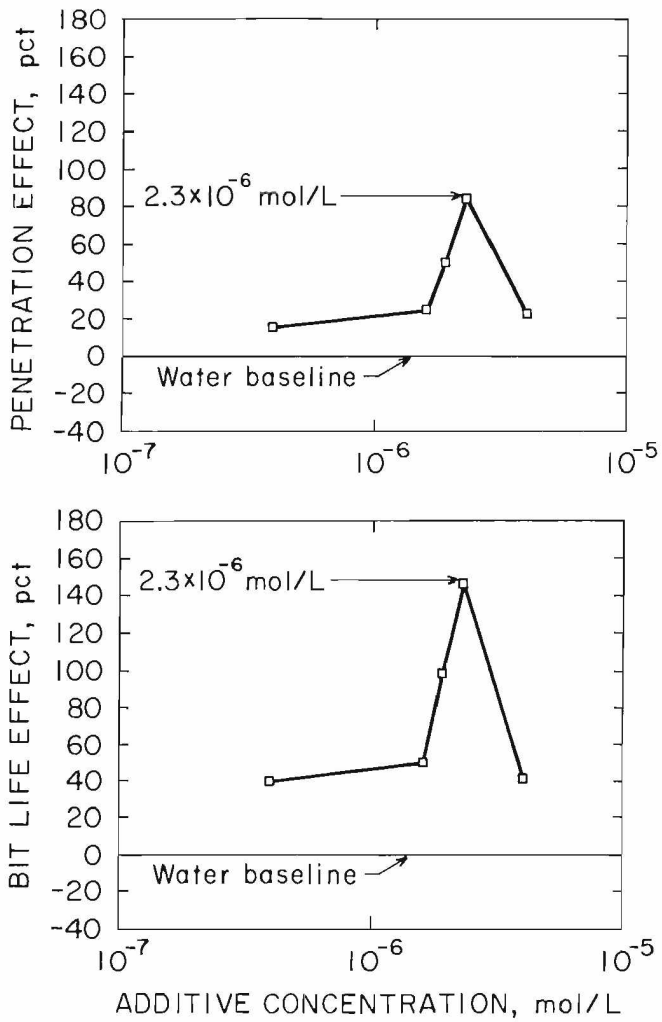

Figure 4.—ZSC control of drilling penetration and bit life in Tennessee marble with $AlCl_3$ in DDIW.

EFFECT OF BIT TYPE ON ZSC-CONTROLLED DRILLING

ZSC-controlled drilling enhancement with diamond-impregnated bits has been demonstrated for Sioux Quartzite, Westerly Granite, and Minnesota taconite. Drilling of Tennessee marble was done with a tungsten carbide spade-type bit to determine whether ZSC-controlled drilling was applicable to other bit types.

As noted by Westwood (*4*), the cutting mechanisms between the diamond coring and tungsten carbide spade bit types are sufficiently different. Conventionally, spade bits as described here are not used in rock drilling, but rather in the machine-tooling trades. However, if a rock is not too hard, it can be drilled with a spade bit, which acts with a scraping or dragging motion. Often the depth of cut for sharp spade bits is greater per pass as compared to diamond bits, all other conditions being equal, but the bits wear down quickly.

The demonstration of successful ZSC-controlled drilling enhancement for both bit types strongly supports the universality of ZSC-controlled drilling with respect to bit type. It is concluded from these results that ZSC-controlled drilling should be universally applicable to all drag bit types and possibly to all drill bit types.

Drilling of Tennessee marble with the diamond-impregnated coring bit was also tried, however, no decline in drilling rate was observed, even after numerous test holes. This meant that any diamond drilling tests using sharp and dull states, as defined by this study, would take too long to be practical in the test program.

EFFECT OF SURFACE CHARGE MODIFIER ON ZSC-CONTROLLED DRILLING

Previous drilling research successfully demonstrated ZSC-controlled drilling enhancement for Sioux Quartzite and Westerly Granite (*5*) using inorganic salts such as $AlCl_3$, $CaCl_2$, NaCl, $ZrCl_4$, and $Al(NO_3)_3$ as surface charge modifiers. Determination of the universality of ZSC-controlled drilling with regard to the type of surface charge modifier required testing of previously tested rock types with other types of surface charge modifiers such as organic cationic surfactants, acid-base solutions, cationic polymers, and nonionic polymers with some cationic character.

Cationic Surfactants

Four cationic surfactants were tested as surface charge modifiers. Three of these surfactants were similar quaternary ammonium bromides; the 12-carbon dodecyltrimethyl ammonium bromide (DTAB), the 14-carbon tetradecyltrimethyl ammonium bromide (TTAB), and the 16-carbon hexadecyltrimethyl ammonium bromide (HTAB). The fourth surfactant was a commercially available low-molecular-weight cationic polymer, of Percol 402. DTAB, TTAB, and HTAB drilling solutions were prepared in DDIW and tested on Sioux Quartzite; therefore, the drilling performances obtained with ammonium bromide additive solutions were compared to the baseline drilling performance for Sioux Quartzite with DDIW. Percol 402 drilling solutions were prepared in Erie Mining mine well water and were tested on Minnesota taconite. Percol 402 drilling performance was therefore compared to the baseline drilling performance for Minnesota taconite with Erie Mining mine well water. Drilling tests were conducted with surfactant solution concentrations below, at, and above the ZSC concentration.

Penetration and bit life effects for DTAB, TTAB, and HTAB in DDIW are given in table 7 and plotted versus surfactant concentration in figures 5 and 6, respectively, for Sioux Quartzite. Drilling with DTAB at a concentration of 9.8×10^{-4} mol/L, which is very near the ZSC concentration of 9.4×10^{-4} mol/L, produced simultaneous maximum increases in penetration and bit life of 118 and 100 pct (figs. 5*A*-6*A*). Penetration effect improvements for TTAB and HTAB at their respective ZSC concentrations of 7.2×10^{-5} mol/L and 1.6×10^{-6} mol/L were both 88 pct (figs. 5*B*-5*C*), while bit life extensions were 87 and 56 pct, respectively (figs. 6*B*-6*C*).

Penetration and bit life effects for Percol 402 are given in table 7 and plotted as a function of concentration in figures 2*C* and 3*C*. Because the exact equivalent molecular weight of Percol 402 was not known, solutions were made up in parts per million as volume per volume. Drilling with the very dilute solutions of Percol 402, which produces the ZSC condition at 0.64 ppm, resulted in the best drilling performance; a 175-pct improvement in penetration effect and a 141-pct improvement in bit life.

It is concluded from the drilling results for cationic surfactants that drilling with ZSC concentration solutions of these surfactants also gives rise to simultaneous maximum penetration effect and maximum bit life.

Acid-Base Solutions

Surface charge neutralization also occurs at the isoelectric point (IEP) that is achieved by adjusting the pH of the water with either acid or base, depending upon whether the IEP-pH is lower or higher than the incipient pH of the water. For magnetite, the IEP pH is about 5.5. Therefore, drilling of Minnesota taconite was conducted with solutions whose pH were above, at, and below the IEP-pH value of 5.5. Penetration and bit life effects are given in table 7 and plotted as a function of pH in figures 2*B* and 3*B*.

Buffer solutions were employed to ensure that the desired pH was maintained throughout the drilling test. This was important since the major chemical byproduct of rock drilling has been found to be hydroxide ions (OH^-). Monitoring the pH of both the influent and effluent streams when drilling with DDIW alone has shown that drilling raises the drilling fluid pH as much as 3 to 4 pH units.

Drilling with a pH 5.5 buffer solution (acetic acid-sodium acetate) resulted in simultaneous increases of 279 pct in penetration and 218 pct in bit life compared to drilling with DDIW alone. One possible explanation for these much higher drilling performance improvements, which are about twice those for drilling Minnesota taconite with ZSC concentration solutions of $AlCl_3$, is that the ZSC condition is maintained throughout the test by the buffer solution. With the ZSC concentration solution of $AlCl_3$, this is probably not the case as the drilling-produced OH^- ions alter or vary the surface charge condition during the course of the drilling test. The results of these tests further point to the universality of ZSC-controlled drilling irrespective of the type of additive employed to neutralize the surface charge.

Cationic Polymer

Because drilling particulates flocculate in a ZSC concentration solution, this flocculation was thought to be partially responsible for the enhanced drilling performance at the ZSC concentration. Therefore, two polymers (one cationic and one nonionic) that flocculate particulates primarily by a molecular bridging mechanism, and secondarily by a charge neutralization mechanism, were tested as drilling fluid additives.

The cationic polymer used as a drilling fluid additive was the water-soluble, high-molecular-weight polyacrylamide (PAA). Drilling solutions of PAA were prepared

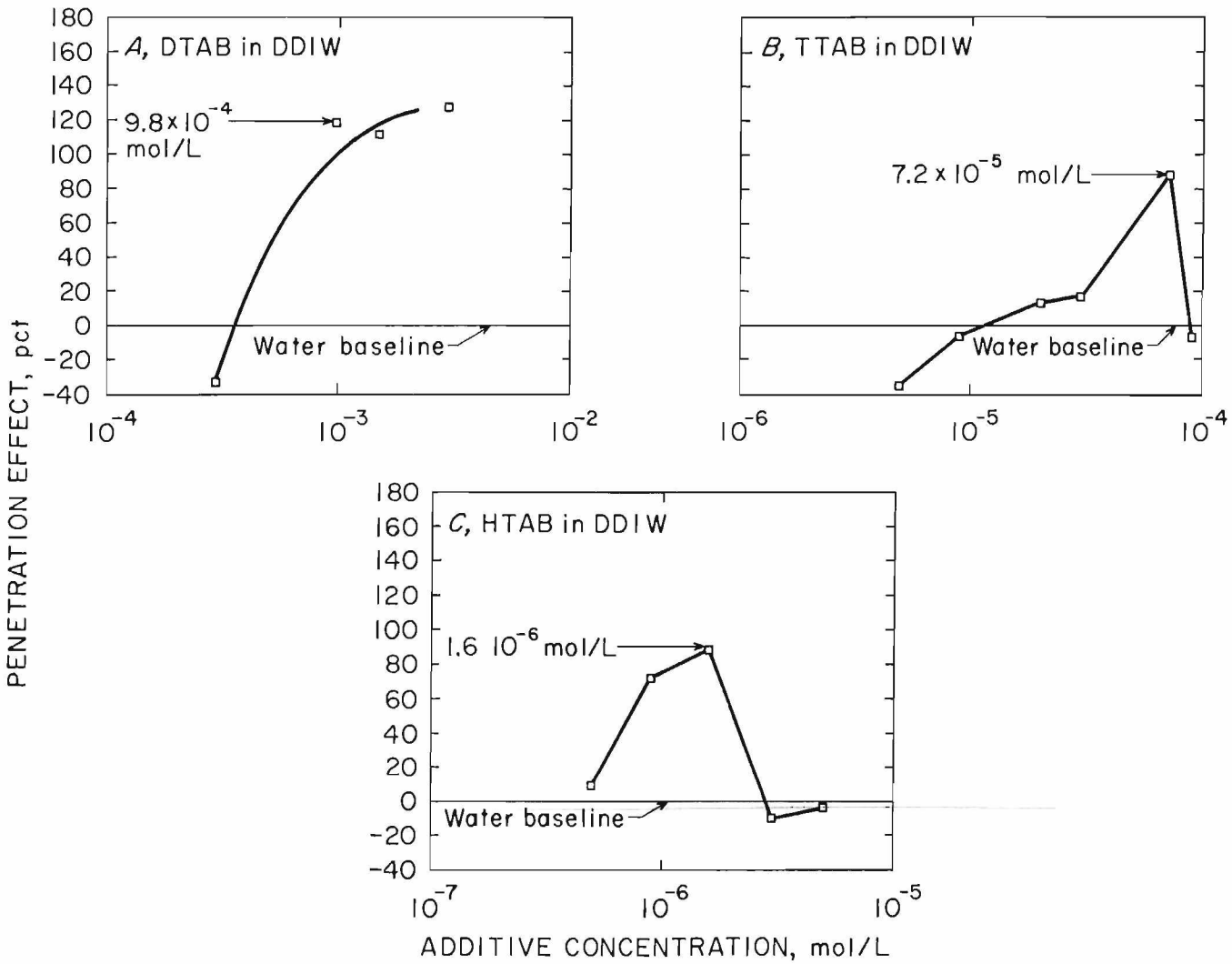

Figure 5.—ZSC control of drilling penetration in Sioux Quartzite with cationic surfactants in DDIW.

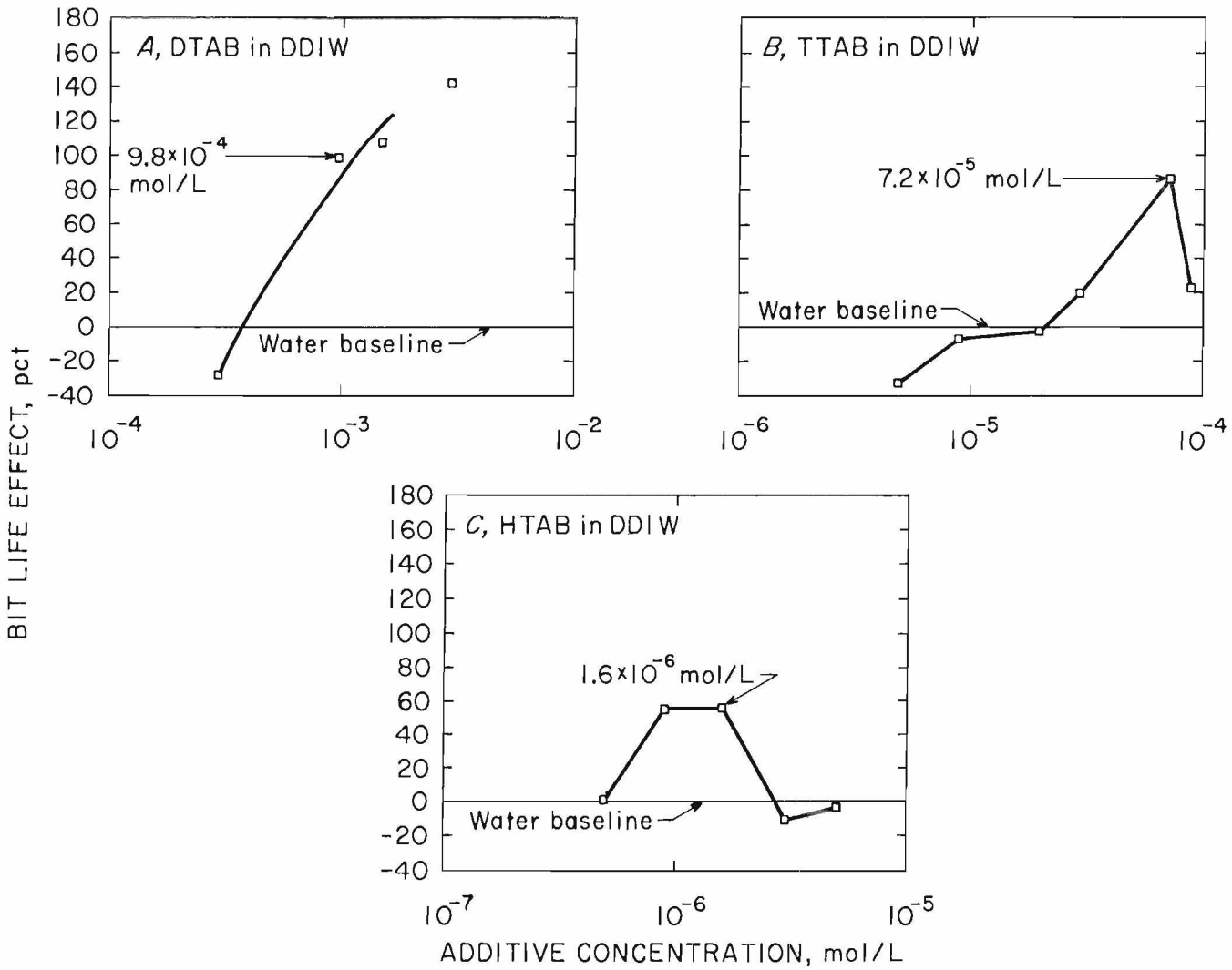

Figure 6.—ZSC control of bit life in drilling Sioux Quartzite with cationic surfactants in DDIW.

in Minneapolis tap water for testing of Sioux Quartzite. The drilling performance of PAA was therefore compared to the baseline drilling performance of Sioux Quartzite in Minneapolis tap water. Solution concentrations of PAA below, at, and above the ZSC concentration were tested. Penetration and bit life effects for PAA are given in table 7 and are plotted as a function of concentration in figures 7*B* and 8*B*.

As with other cationic additives, drilling with the ZSC concentration of PAA (0.25 ppm) produced simultaneous maximum increases in penetration and bit life effects, 334 pct and 187 pct, respectively. A possible explanation for the outstanding improvements in penetration and bit life effects for PAA, as compared to other cationic additives, may be found in the fact that a ZSC concentration solution of PAA could constitute a non-Newtonian fluid with its contingent effects.

Rotation of a drill against a rock in a non-Newtonian fluid should result in a reduction of the thickness of the rock-water interfacial double layer (*9*). This condition promotes a much more efficient transfer of energy from the drill to the rock across the solution-rock interface. Thus, under constant mechanical energy input conditions there is more energy available at the rock surface for fragmentation purposes and increased penetration is observed.

It should be noted that the PAA drilling results (figs. 7*B*-8*B*) clearly indicate that flocculation is not responsible for enhanced ZSC-controlled drilling. While flocculation with PAA occurs at all concentration levels above 0.1 ppm, the enhanced drilling performance is achieved only at the ZSC concentration of 0.25 ppm. The results of these tests with the cationic polymer also indicate the universality of ZSC-controlled drilling irrespective of the type of additive employed to neutralize the surface charge.

Nonionic Polymer

The nonionic polymer used as a drilling fluid additive was the water-soluble, high-molecular-weight compound, PEO. Drilling solutions of PEO were prepared in Minneapolis tap water for testing Sioux Quartzite and in Erie Mining mine pond water for testing Minnesota taconite, using 5 million molecular weight (MW) PEO. The drilling performance of PEO was compared to the respective baseline drilling performance for Sioux Quartzite in Minneapolis tap water and Minnesota taconite in Erie Mining mine pond water. Although PEO is available in a range of molecular weights from 0.1 to 6 million, drilling tests were only conducted with the 5 million MW PEO. ZSC concentrations (parts per million) of these other PEO molecular weight varieties, however, were also determined and found to be the same as the ZSC concentration of the 5 million MW PEO. Penetration and bit life effects for PEO in drilling Sioux Quartzite (figs. 7*C*-8*C*) and Minnesota taconite (figs. 2*D*-3*D*) are given in table 7.

PEO is an unusual surface charge modifier. Because it is nominally nonionic, PEO would not be expected to neutralize the rock surface charge and therefore produce enhanced ZSC-controlled drilling. In fact, zeta potential determinations of Sioux Quartzite particles in the commercial low-molecular-weight nonionic surfactants, Tergitol NPX and Surfynol 465, and the high-molecular weight nonionic polymer, hexaethyl cellulose, showed that they had no effect on the surface charge of the Sioux Quartzite particles at any concentration. Zeta potential determinations of Sioux Quartzite particles in solutions of ever-increasing PEO concentration, however, showed that PEO, like the cationic additives (inorganic salts, cationic surfactants, and cationic polymers) brought the zeta potential from an initial negative value to zero but, unlike the cationic additives, did not produce a positive zeta potential at higher concentrations. Instead, at higher PEO concentrations the zeta potential remained at zero; i.e., the ZSC condition was maintained.

The ability of PEO to neutralize the rock surface charge then must be due to the electronegativity differences of the atoms in the ethylene oxide units of the PEO molecule. PEO is hydrated in aqueous solutions by hydrogen bonding between water molecules and the ether oxygens of the PEO chains, which consequently establishes induced dipoles in each water molecule. Even though PEO is considered a nonionic polymer, water bonded to the polymer creates a partial positive charge at the end of the water molecules not bonded to the polymer because of electron deficiency, that is, the induced dipole. This induced positive character acts on a rock surface to occupy the inner Helmholtz plane of the electric double layer on the solid-liquid interface thus neutralizing the intrinsic charge on the rock surface.

Most rocks found in nature have a negative surface charge in water. The positive dipoles associated with the hydrated PEO polymer are able to neutralize the intrinsic negative charge on these rocks. It is the partially negative dipoles of the polymer's etherial oxygens that most likely neutralize an intrinsic positive charge on a rock. This behavior was demonstrated when testing the zeta potential response of magnesium oxide (MgO) to PEO solutions made with DDIW. The MgO surface charge, which is intrinsically positive in water, was also neutralized by PEO solutions.

There are a number of additional inherent factors involved in the use of PEO polymer in solution. PEO solutions also behave as non-Newtonian fluids, even at dilute concentrations. One of the effects of non-Newtonian fluids, as mentioned previously, is that the thickness of the double layer at the rock surface is reduced. This would increase the efficiency of energy transfer to the drill, resulting in greater cutting efficiency.

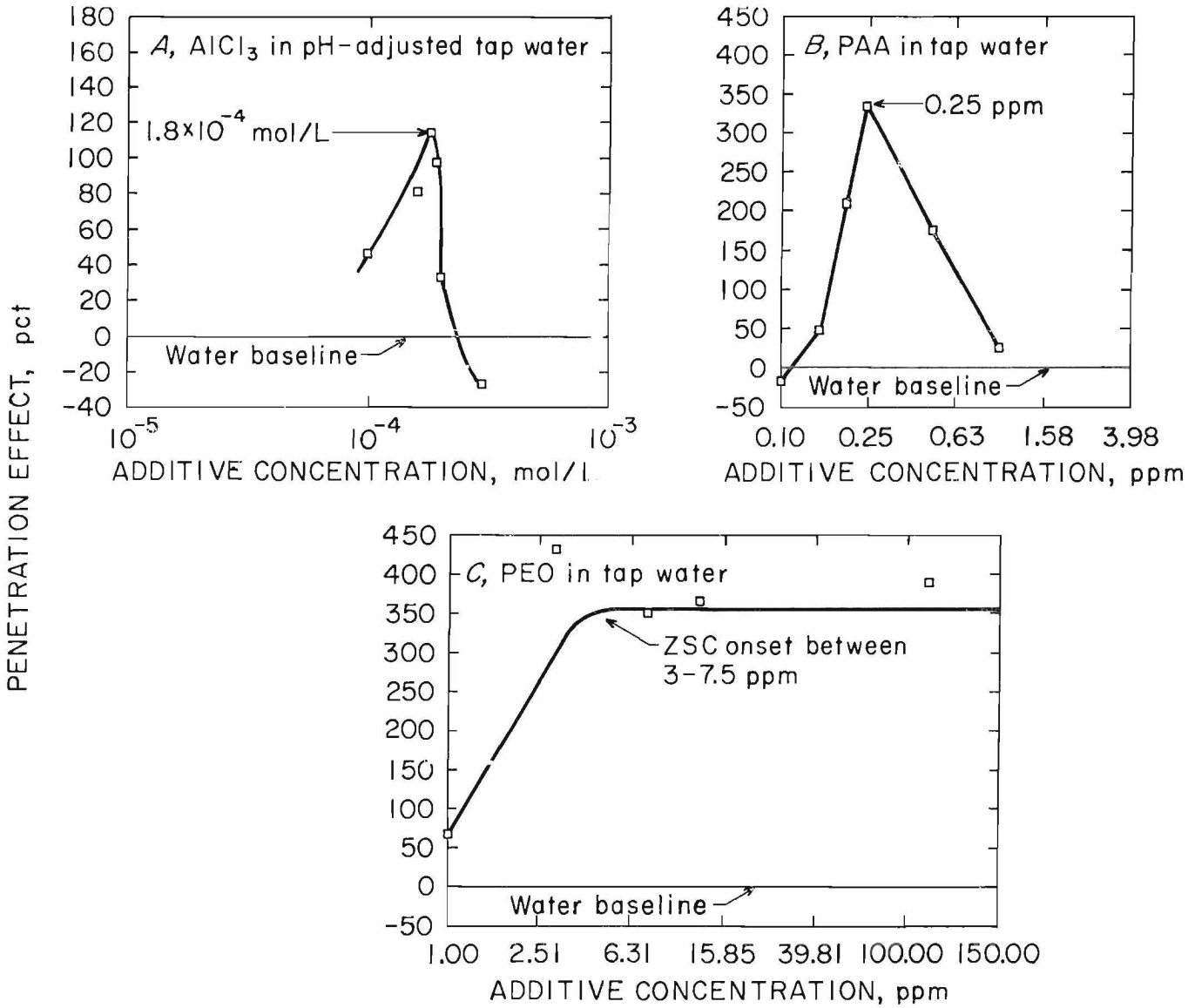

Figure 7.—ZSC control of drilling penetration in Sioux Quartzite with $AlCl_3$, PAA, and PEO in tap water.

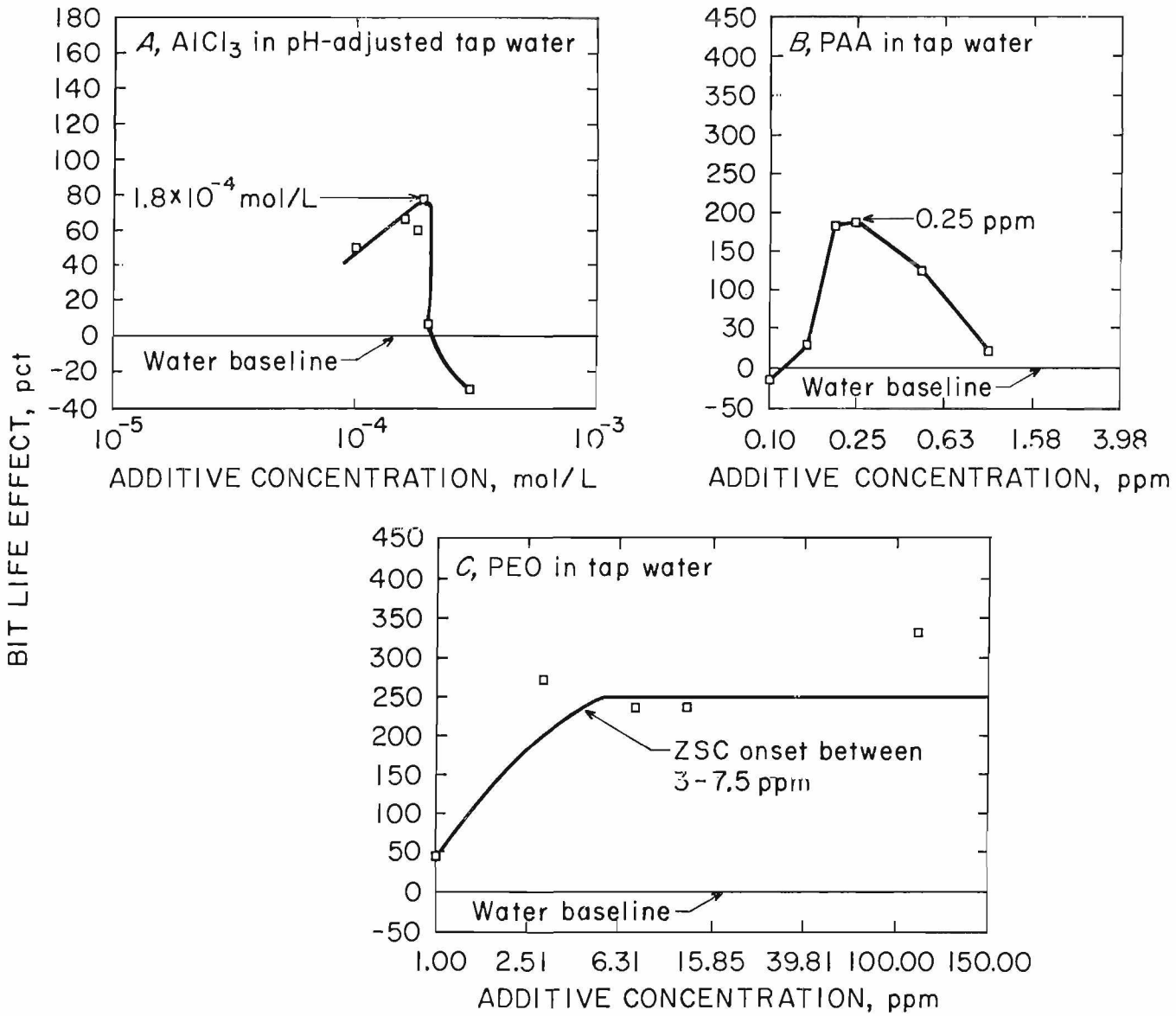

Figure 8.—ZSC control of bit life in drilling Sioux Quartzite with $AlCl_3$, PAA, and PEO in tap water.

Secondly, hydrogen bonding in PEO solutions produces a very stable zero zeta-potential condition between the fluid and the rock. In comparison, as seen by the use of cationic additives, the enhanced drilling phenomenon was very concentration specific. The concentration of the additive needed to be almost precisely at the zero zeta potential concentration to yield an increased drilling effect with any deviation in the composition of the water or the rock or the concentration of the additive diminishing the effect.

With cationic additives, the systems that could tolerate only a very small change in ZSC concentration produced a minor, albeit significant, drilling increase. For example, $AlCl_3$ in DDIW produced 100 to 150 pct improvements. Other cationic systems that could tolerate some deviation from ZSC concentration, such as with the acid-buffered solutions, demonstrated even greater improvements around 175 to 275 pct. This indicates that as chemical systems can self adjust to compositional changes in the water and rock while maintaining the zero zeta-potential condition, drilling efficiencies would be improved. Because PEO solutions (above a minimum concentration) are able to maintain a stable zero zeta-potential condition regardless of changes in fluid and rock chemistry, PEO solutions therefore have the inherently superior ability to self adjust. (This is ideal for usage in field drilling.)

Lastly, the high-molecular-weight, long chains of this polymer not only increase the hydrodynamic flow characteristics of the fluid, they also increase the efficiency of cuttings removal, and probably provide some lubricative quality to the solution as well. None of these effects were evident with the use of the cationic additive solutions.

Comparing PEO drilling plots of the penetration and bit life effects as a function of concentration for Sioux Quartzite (figs. 7*C*-8*C*) or Minnesota taconite (figs. 2*D*-3*D*) with similar plots using cationic surfactants and inorganic salts (figs. 2-3, 5-6) shows why PEO is the best drilling performance enhancer. For Sioux Quartzite, penetration effects of over 350 pct and bit life effects of over 235 pct were attained with PEO. For Minnesota taconite, penetration effects of over 650 pct and bit life effects of over 400 pct were attained with PEO. The penetration and bit life effects obtained with ZSC concentration solutions of the cationic surfactants or inorganic salts were much less. In addition, there is a wide range of concentrations of PEO that produce a maximum penetration effect compared to the single concentration of cationic additives that produces the maximum penetration effect.

It is concluded on the basis of the tests with PEO that it is the best additive for accomplishing ZSC-controlled drilling. Not only does it produce the enhanced ZSC drilling phenomenon over a wide range of concentrations, it also produces much greater improvements in bit life and penetration. It is further concluded on the basis of the tests with PEO and the cationic additives that establishment of the ZSC condition is the most important factor in enhanced drilling.

EFFECT OF DRILLING FLUID WATER ON ZSC-CONTROLLED DRILLING

Previous drilling research successfully demonstrated ZSC-controlled drilling enhancement for Sioux Quartzite and Westerly Granite (*5*) using inorganic salt solutions in DDIW. DDIW was used as the baseline-comparison water to clearly show any additive effect without additional ions such as those found in tap water or mine water masking the effect. Determination of the universality of ZSC-controlled drilling with regard to water type required testing of previously tested rock types with other water types, such as tap water and mine water. While the pH of the DDIW used in ZSC-controlled drilling research was constantly in the range 5.3 to 6.0, the pH of Minneapolis tap water ranged from 7.3 to 7.7 and the pH of Erie Mining mine pond and well waters ranged from 7.0 to 7.5 and 7.9 to 8.0, respectively. Therefore, in using $AlCl_3$ as the additive in tap water or in either of the mine waters, a pH adjustment of these waters was required before $AlCl_3$ was added to prevent precipitation and flocculation of the Al^{+3} ions in solution as aluminum hydroxide $Al(OH)_3$. Acidifying the tap water to pH 3.8 with HCl resulted in only a negligible decline in drilling performance on Sioux Quartzite compared to plain tap water without the addition of acid.

Penetration and bit life effects for drilling Sioux Quartzite with $AlCl_3$ solutions made from acidified tap water compared to acidified tap water drilling are given in table 7 and graphically displayed in figures 7*A* and 8*A*. Drilling with the ZSC concentration of 1.8×10^{-4} mol/L $AlCl_3$ in pH-adjusted tap water resulted in maximum simultaneous increases of 113.6 pct in penetration and 59.6 pct in bit life compared to pH-adjusted tap water alone. These increases showed that enhanced drilling performance could also be obtained with acidified tap water. The ZSC concentration of $AlCl_3$ in DDIW is 7×10^{-7} mol/L; however, in plain tap water it is 4.5×10^{-5} mol/L, and in pH-adjusted tap water it is 1.8×10^{-4} mol/L. The concentration of 4.5×10^{-5} mol/L $AlCl_3$ in plain tap water can only be maintained for a short duration. The basic pH condition produces a short-lived metastable ZSC condition because the basic pH condition of the plain tap water flocculates the aluminum ions as hydroxides in a few hours. These differences in concentration needed to achieve the ZSC condition are most likely due to the ions present in the tap water because the ionic strength of a solution affects the surface electrical double layer (the double layer is an equilibrium phenomenon.)

The zeta potential for Sioux Quartzite in DDIW is -25.6 mV while the zeta potentials for Sioux Quartzite in plain and pH-adjusted tap water are -33.0 and -26.5 mV, respectively (table 5). The more negative zeta potential in plain tap water indicates more intrinsic negative charge on the rock surface to be neutralized and thus a greater amount of Al^{+3} required. While the pH adjustment of the tap water raises the zeta potential from -33.0 mV to -26.5 mV, and thus it would appear that while less Al^{+3} ions should be required for surface charge neutralization, an overall increase in Al^{+3} ions is actually required to neutralize the anion component of the added acid. One advantage of drilling with $AlCl_3$ solutions prepared using tap water instead of DDIW is that the ZSC-concentration peak is broader, allowing some flexibility in solution concentration.

It is concluded on the basis of these data, and that for drilling Minnesota taconite with Percol 402 and PEO solutions (figs. 2-3) in mine well water and mine pond water, respectively, and Sioux Quartzite with PAA and PEO solutions in tap water (figs. 7-8), that ZSC-controlled drilling is universally applicable with respect to any drilling fluid water characteristics.

SUMMARY AND CONCLUSIONS

ZSC-controlled drilling performance has been investigated to determine the boundary conditions for enhanced drilling rates and bit life. Laboratory drilling tests were performed on Minnesota taconite, Tennessee marble, and Sioux Quartzite using diamond-impregnated coring bits or tungsten carbide spade bits. Drilling fluids were prepared from chemical additives such as inorganic salts, cationic surfactants, cationic polymers, acids, or nonionic polymers in either DDIW, mine water, or tap water at concentrations below, at, and above the ZSC concentration. These tests have established the universality of ZSC-controlled drilling performance with respect to rock type, type of bit, surface charge modifier, and drilling fluid water composition.

Previous enhanced ZSC-controlled drilling performance observed in drilling the high silicate rocks, Sioux Quartzite and Westerly Granite, has also been attained with a moderate silicate rock, Minnesota taconite, and a nonsilicate rock, Tennessee marble, thereby establishing that the enhanced drilling performance at ZSC condition is independent of silica content of the rock.

The enhanced drilling performance at ZSC conditions occurred for the diamond-impregnated core drilling of Sioux Quartzite, Westerly Granite (*5-6*), and Minnesota taconite; and the tungsten carbide spade bit drilling of Tennessee marble. Further testing with percussive and rotary tricone bits will be needed to determine the universality this affect to all bit types.

Enhanced drilling performance has been obtained with solution concentrations of inorganic salts, cationic surfactants, cationic polymers, acids, and nonionic polymers with some cationic or hydrogen-bonding character. All of these additives neutralized the rock surface charge, thereby establishing that the ZSC condition is the important factor in ZSC-controlled drilling and not the type of surface charge modifier.

Enhanced drilling performance was achieved with DDIW, mine water, and tap water. Because of the increased amounts of anions in the mine and tap waters, more additive was required for surface charge neutralization when using these waters in place of DDIW.

Maximum penetration improvements obtained for additives compared to baseline water penetration results ranged from 84 pct for Tennessee marble drilled with a ZSC concentration of $AlCl_3$ in DDIW to over 650 pct for Minnesota taconite drilled with a wide range of ZSC concentrations of PEO in mine water. Maximum bit life improvements obtained for additives compared to baseline water bit life results ranged from 56 pct for Sioux Quartzite drilled with a ZSC concentration of HTAB in DDIW to over 400 pct for Minnesota taconite drilled with a wide range of ZSC concentrations of PEO in mine water.

The best additive for accomplishing ZSC-controlled drilling is PEO, a nominally nonionic polymer with partial cationic character (polarizable structure) in aqueous solutions. Unlike the cationic additives and acid solutions that achieve the ZSC condition at only one concentration or pH value, respectively, PEO maintains the ZSC condition over a wide range of concentrations because of its polarizable structure. Thus, with PEO the criticality of the solution concentration during drilling is greatly diminished. In addition, PEO results in much greater improvements in bit life and penetration than the cationic additives.

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